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- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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(54) Title: VANADIUM CATALYSTS AND PROCESS FOR THE DIRECT CONVERSION OF METHANE INTO ACETIC ACID



(I)

(57) Abstract: The invention consists on the utilization of complexes of vanadium (in the +4 and +5 oxidation states) with bi- or poly-dentate ligands coordinated by nitrogen and oxygen (N,O) or by oxygen

and oxygen (O,O) atoms, namely derivatives of aminoalcohols, (hydroxyimino)dicarboxylic acids, hydroxypyranones, trifluoroacetic acid, triflic acid or inorganic acid, as catalysts for the direct single-pot conversion, under mild conditions, of methane in acetic acid, either in the absence or in the presence of carbon monoxide, and in the presence of a peroxodisulfate salt ($\text{K}_2\text{S}_2\text{O}_8$), in trifluoroacetic acid (CF_3COOH), according to the general reaction (I).

INTERNATIONAL SEARCH REPORT

national Application No

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A. CLASSIFICATION OF SUBJECT MATTER	IPC 7 B01J31/04 B01J31/18 B01J31/22 B01J31/26 B01J31/36
	C07C51/145

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>TANIGUCHI Y ET AL: "Highly Efficient Vanadium-Catalyzed Transformation of CH₄ and CO to Acetic Acid" ORGANIC LETTERS, ACS, WASHINGTON, DC, US , vol. 1, no. 4, 8 July 1999 (1999-07-08), pages 557-559, XP002286128 cited in the application the whole document</p> <p>---</p>	1-4
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		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- *&* document member of the same patent family

Date of the actual completion of the International search

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INTERNATIONAL SEARCH REPORT

national Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Relevant to claim No.	
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A	EP 0 560 656 A (SUMITOMO CHEMICAL CO) 15 September 1993 (1993-09-15) claims; examples ---	1-4
A	ASADULLAH M ET AL: "One-step carboxylation reaction of saturated hydrocarbons with CO by Co(OAc) ₂ catalyst under mild conditions" APPLIED CATALYSIS A: GENERAL, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 194-195, 13 March 2000 (2000-03-13), pages 443-452, XP004272248 ISSN: 0926-860X the whole document ---	1-4
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INTERNATIONAL SEARCH REPORT

National Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BERRY R E ET AL: "The Structural Characterization of Amavadin" ANGEWANDTE CHEMIE. INTERNATIONAL EDITION, WILEY-VCH VERLAG, WEINHEIM, DE , vol. 38, no. 6, 15 March 1999 (1999-03-15), pages 795-797, XP002286132 cited in the application the whole document ---	3
A	CARAVAN P ET AL: "Reaction Chemistry of BMOV, Bis(maltolato)oxovanadium(IV)-A Potent Insulin Mimetic Agent" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, US , vol. 117, no. 51, 27 December 1995 (1995-12-27), pages 12759-12770, XP002286133 cited in the application page 12759 -page 12760; figures 1,2 ---	3
A	CHEN C-T ET AL: "Catalytic Nucleophilic Acyl Substitution of Anhydrides by Amphoteric Vanadyl Triflate" ORGANIC LETTERS, ACS, WASHINGTON, DC, US , vol. 3, no. 23, 20 October 2001 (2001-10-20), pages 3729-3732, XP002286134 cited in the application the whole document ---	3
A	HAMSTRA B J ET AL: "Structural and Solution Characterization of Mononuclear Vanadium(IV) Complexes That Help To Elucidate the Active Site Structure of the Reduced Vanadium Haloperoxidases" INORGANIC CHEMISTRY, AMERICAN CHEMICAL SOCIETY. EASTON, US, vol. 36, no. 21, 8 October 1997 (1997-10-08), pages 4866-4874, XP002286135 cited in the application page 4866 -page 4867 ----	3
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INTERNATIONAL SEARCH REPORT

National Application No
CN/T/PT 03/00015

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>REIS P M ET AL: "Single-Pot Conversion of Methane into Acetic Acid in the Absence of CO and with Vanadium Catalysts Such as Amavadine" ANGEWANDTE CHEMIE. INTERNATIONAL EDITION, WILEY-VCH VERLAG, WEINHEIM, DE , vol. 42, no. 7, 17 February 2003 (2003-02-17), pages 821-823, XP002286136 the whole document</p> <p>-----</p>	1-4
T	<p>CRANS D C ET AL: "The Chemistry and Biochemistry of Vanadium and the Biological Activities Exerted by Vanadium Compounds" CHEMICAL REVIEWS, AMERICAN CHEMICAL SOCIETY. EASTON, US, vol. 104, no. 2, 29 January 2004 (2004-01-29), pages 849-902, XP002286137 page 873</p> <p>-----</p>	

INTERNATIONAL SEARCH REPORT
Information on patent family members

national Application No

PT/PT 03/00015

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